

## Amendments to the Specification

Please replace paragraph [0002] of the specification with the following paragraph:

**[0002]** The present application is related to U.S. application Serial No. 09/397,814 filed September 17, 1999, now U.S. Patent No. 6,806,295, incorporated herein by reference.

Please replace paragraph [0004] of the specification with the following paragraph:

**[0004]** Zirconium titanate (ZT)-based ceramic materials (in the form of solid solutions) have many unique properties such as high resistivity, high dielectric constant (thus providing high charge storage capacity), high permittivity at microwave frequencies, and excellent temperature stability of microwave properties. They have extremely wide applications such as in microwave telecommunications (as capacitors, dielectric resonators in filters and oscillators) and in catalysis as effective acid-base bi-functional catalysts and photocatalysts. In the form of thin films, they also find advanced applications in piezoelectric sensors, transducers, ultrasonic motors, hydrocarbon sensors, integrated microwave devices, refractory materials, high-temperature pigments, composites for high-temperature corrosive environments, and thin-film optics. In addition, ZT powders (crystalline  $Zr_xT_{1-x}O_4$ ) can be good precursor materials for synthesis of other valuable electroceramics such as lead zirconate titanate (PZT) or lanthanum doped PZT (PLZT) (~~Chen et al., 1999, Cerqueira et al., 1998, see,~~

Chen et al., "Hydrothermal Synthesis and Characterization of Crystalline  $Zr_xT_{1-x}O_4$  . . . ", *J. Mater. Sci.*, 1999, 1379-1383, 34; and Cerqueira et al., "Synthesis and Characterization of PLZT (9/65/35) by the Pechini Method and Partial Oxalate", *Mater. Lett.*, 1998, 166-171, 35, both references incorporated herein by reference). PZT is the most used electroceramic material in industrial applications as actuators and transducers.

Please replace paragraph [0005] of the specification with the following paragraph:

**[0005]** As is true for many other materials, ultrafine-grained, high quality powders of ZT are in high demand. Fine powders are necessary precursors for making monolithic ceramics via casting as well as ceramic films via coating process. For such a binary (two metal elements) oxide system, compositional homogeneity and microstructure uniformity (low or no phase segregation) are very important. It is well known that powder characteristics such as particle size, shape, size distribution, agglomeration, crystallite size, chemical and phase composition, determine to a large extent, the microstructures developed during sintering and thus affect the properties of ceramic materials. On the other hand, it is necessary to use fine and single phase ZT powder to obtain fine and sinterable PZT powders by the partial oxalate method (Cerqueira et al., "Synthesis of Ultra-fine Crystalline  $Zr_xT_{1-x}O_4$  Powder by Polymeric Precursor Method", *Mater. Lett.*, 1995, 181-185, 22).

Please replace paragraph [0007] of the specification with the following paragraph:

**[0007]** Among the aforementioned synthesis routes, few could produce ultrafine powders containing aggregation-free, monodispersed, microsphere particles. Some routes such as the classical sol-gel process and some polymeric precursor methods involve the use of expensive metal alkoxide salt(s) or commercially unavailable metallorganic salts. Most routes, such as gel-forming via precipitation or polymeric precursor methods, still require the undesirable procedure of grinding dried gels into powders with no control of particle shape. Irregular shaped powdered ceramic particles are both difficult to handle and use on an industrial scale and thus spherical particles are preferred for many distinct advantages. The submicron, spherical particles reported by Hirano et al. at "Chemical Processing and Microwave Characteristics ...", J. Am. Ceram. Soc., 74, 1320-24, (1991), obtained by controlled hydrolysis of metal alkoxides, are agglomerated. Bhattacharya et al. "Sol Gel Preparation, Structure and Thermal Stability of Crystalline Zirconium Titanate Microspheres", J. Mater. Sci. 31, 267-271, (1996), produced dispersed, sphere-shaped particles; however, the size of the reported "microspheres" was in the range of 15-50  $\mu\text{m}$ , which is quite large for applications that require ultrafine particles (i.e., submicron to a few micrometers in diameter).

Please replace paragraph [0016] of the specification with the following paragraph:

**[0016]** Fig. 1a shows a SEM scanning electron microscope (SEM) photograph of ultrafine microspheres of  $\text{ZrO}_2$  particles under the following conditions: zirconyl chloride

( $\text{ZrOCl}_2$ ) = 0.1 M, volumetric ratio of alcohol to aqueous part (RH) = 3/1, temperature (T) = 100° C., time (t) = 24 hr, hydroxyl propyl cellulose (HPC) =  $2.0 \times 10^{-3}$  g/cm<sup>3</sup>.

Please replace paragraph [0033] of the specification with the following paragraph:

**[0033]** Fig. 6 shows a typical ~~RTXRD~~ room-temperature X-ray diffraction (RTXRD) spectrum of as-prepared ZT microsphere particles made under the following sample preparation conditions: C = 0.1 M, RH = 1/1 to 5/1, T = 100° C, t = 24 hr, HPC =  $2.0 \times 10^{-3}$  g/cm<sup>3</sup>, see Fig. 3 for SEM images.

Please replace paragraph [0034] of the specification with the following paragraph:

**[0034]** Fig. 7 shows ~~HTXRD~~ high-temperature X-ray diffraction (HTXRD) spectra during in-situ calcinations of ZT microsphere particles under the following sample preparation conditions: C = 0.025 and 0.2 M, RH = 3/1, T = 100° C, t = 24 hr, HPC =  $2.0 \times 10^{-3}$  g/cm<sup>3</sup>, wherein above ~ 600°C, peaks characteristic of single  $\text{ZrTiO}_4$  phase are present.

Please replace paragraph [0035] of the specification with the following paragraph:

**[0035]** Fig. 8a shows ~~TGA/DTA~~ thermogravimetric analysis / differential thermal analysis (TGA/DTA) analysis of ZT samples from various conditions with varying metal salt concentrations from 0.025 to 0.2M.

Please replace paragraph [0037] of the specification with the following paragraph:

**[0037]** Fig. 9a is a high-resolution ~~TEM~~ transmission electron microscope (TEM) image of a ZT microsphere wherein Point D is in the resin for TEM sample preparation; sample synthesis conditions: C = 0.1 M, RH = 2/1, T=100°C, t = 24 hr, HPC =  $2.0 \times 10^{-3}$  g/cm<sup>3</sup>.

Please replace paragraph [0045] of the specification with the following paragraph:

**[0045]** Characterization of particle samples. The evolution of particle size and morphology, with reaction time was analyzed by SEM (JSM-T220A, JEOL) in which the particles were spread and air-dried on conductive carbon tape that was attached to a cylindrical brass stub. The particles on the stub were plasma coated with gold (Hummer 6.2 sputtering system, Anatech LTD) for 3-4 min in preparation for SEM imaging. Room-temperature X-ray diffraction (RTXRD, Scintag) was used for phase identification and analysis of crystallite size in the oxide powder samples. The crystallization process of the amorphous powders and the phase transformation in the temperature range of 27 to 1200° C. were monitored in real time by a HTXRD (for detailed instrument description, see Hu et al., J. Am. Ceram. Soc. 82, 2313, 1999, incorporated herein by reference). Complementary DTA/TGA was also performed (alumina crucible, sample weight 100 mg) using the following conditions: heating rate, 5°C./min; peak temperature, 1250° C; and air flow, 100 cm<sup>3</sup>/min. Specific surface areas of dried

powder samples were analyzed using a nitrogen adsorption analyzer (Micromeritics, Atlanta, Ga.).

Please replace paragraph [0046] of the specification with the following paragraph:

**[0046]** Single oxide precursor particles for zirconia and titania, which were used as a control test, are shown in Fig. 1. The dielectric-tuning precipitation method has previously proven successful for the production of single-metal oxide precursor particles (see, Hu et al., "Sol-Gel and Ultrafine Particle Formation via Dielectric Tuning of Inorganic Salt-Alcohol-Water Solutions", *Journal of Colloid and Interface Science*, **222**, 20-36, 2000 2000a; Park et al., "Effect of Solvent on Titania Particle Formation and Morphology in Thermal Hydrolysis of  $\text{TiCl}_4$ ", *J. Am. Ceram. Soc.* **80**, 743-49, 1997; Moon et al., "Preparation of Monodisperse and Spherical Zirconia Powders by Heating of Alcohol-Aqueous Salt Solutions," *J. Am. Ceram. Soc.* **78**(4):1103-1106, 1995).

However, at the time of this earlier work, it was unknown if such a method could apply to the synthesis of binary metal oxides, in particular the production of ultrafine ZT precursor particles due to unknown factors as inhomogeneous composition or crystalline-phase segregation occurring during coprecipitation of mixed salts, due to different precipitation/crystallization kinetics. The process parameters for ZT synthesis include initial metal salt concentration (C, Zr/Ti molar ratio fixed at 1), isopropanol content in solution (RH ratio, a volume ratio of alcohol to aqueous solution), temperature (T), incubation heating time (t), and HPC concentration (fixed at  $2.0 \times 10^{-3} \text{ g/cm}^3$  for use in this study). Results shown in Fig. 2 clearly demonstrate that near-monodispersed

microspheres of binary oxide (ZT) precursor particles can be produced when both zirconium chloride and titanium tetrachloride are mixed at equimolar concentrations in the initial synthesis solutions. The significant effect of the initial metal ion concentration in mixed solutions on the particle size is also shown in Fig. 2. With increases in metal salt molar concentration from 0.025 M to 0.2 M, the ZT-precursor particle size increased from submicrometer range to a few micrometers in diameter (Fig. 2). In addition, the RH ratio affects not only the size of particles but also their agglomeration state (Fig. 3). At a low RH ratio (1/1), particles show wide size distribution and are somewhat agglomerated (with an observed neck connection between microspheres). With higher RH ratios (up to 5/1), the particles obtained tend to become smaller and better dispersed.

Please replace paragraph [0049] of the specification with the following paragraph:

**[0049]** HTXRD data (Fig. 7) show that crystallization from amorphous precursor particles occurred around 600°C, which agrees well with earlier reported values for amorphous ZT materials from sol-gel synthesis (Sham et al., "Zirconium Titanate from Sol-Gel Synthesis: Thermal Decomposition and Quantitative Phase Analysis", *J. Solid State Chem.* **139**, 225-32, 1998), from a polymer precursor route (Bianco et al., "Zirconium Titanate Microwave Dielectrics Prepared via Polymeric Precursor Route", *J. Eur. Cer. Soc.* **19**, 959-963, 1999), and from high-energy dry ball milling of equal molar ZrO<sub>2</sub>-TiO<sub>2</sub> powder mixture (Stubicar et al., "Microstructure Evolution of an Equimolar Powder Mixture of ZrO<sub>2</sub>-TiO<sub>2</sub> ...", *J. Alloys and Compounds*, **316**, 316-320, 1999).

Single-phase  $\text{ZrTiO}_4$  (orthorhombic, *Pbcn* 60, disordered form, JCPDS 34-0415, lattice parameters:  $a = 0.5035$ ,  $b = 0.5487$ , and  $c = 0.4801$ ) evolved when the sample powder heated up to  $\sim 600^\circ\text{C}$  and also remained after the sample was cooled to room temperature ( $27^\circ\text{C}$ ). It is generally believed that the cations  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  are randomly distributed within the lattice. Based on the phase diagram of the system  $\text{TiO}_2\text{-ZrO}_2$  (Bateman and Notis, "CAD Representation of the Systems  $\text{ZrO}_2\text{-MgO-TiO}_2$  and ...", *Physica B*, 150, p.122-128, 1988), both baddeleyite and ZT solid solution are expected at room temperature for  $\text{Zr/Ti} = 1:1$ ; however, the work of the present invention confirmed that no monoclinic zirconia is present in the sample. The HTXRD crystallization evolution spectra are similar for ZT powders from both synthesis concentrations (0.025 and 0.2 M).

Please replace paragraph [0050] of the specification with the following paragraph:

**[0050]** DTA/TGA data for samples obtained from various conditions are shown in Figs. 8(a) and 8(b). The TGA plots show that slower coprecipitation rate conditions (i.e., at lower salt concentration and lower RH) seem to generate less hydrated amorphous materials (and less shrinkage and weight loss). The large endothermic peak in the DTA plots (below  $200^\circ\text{C}$ ) can be ascribed principally to water elimination from the pores of the particles. The exothermic peak around  $200\text{-}400^\circ\text{C}$  (and some smaller peaks up to  $\sim 500^\circ\text{C}$ ) could be due to the progressive removal of water molecules bonded into the pores of the solid plus the elimination of alcohol coupled in the particle during the coprecipitation. The significant sharp exothermic peak exhibited at temperatures



varying from 530 to 680°C, depending on the concentration and RH (see inserts of DTA plots in Fig. 8a and Fig. 8b), corresponds to the crystallization temperature from amorphous to ZrTiO<sub>4</sub> orthorhombic crystal. The lowest crystallization temperature for the samples of the present invention was around 530°C. It is known that chemical processing influences the thermal crystallization behavior of ZT materials. Navio et al. (see, "Formation of Zirconium Titanate Powder from a Sol-Gel Prepared Reactive Precursor", *J. Mater. Sci.* 27, 2463-2467, 1992; "On the Influence of Chemical Processing in the Crystallization", *J. Mater. Sci. Lett.*, 11, 1570-1572, 1992; and "Thermal Evolution of (Zr,Ti)O<sub>2</sub> Gels Synthesized At Different Basic pH", *J. Therm. Anal.* 40, 1095-1102, 1993 1992a, 1992b, 1993) found that the formation of peroxo species of Ti and Zr seems to enhance the crystallization of ZrTiO<sub>4</sub> at a lower temperature, possibly because the peroxo bonding is broken easily after the thermal treatment. In the work of the present invention, the shifts in crystallization peak clearly indicate that synthesis conditions (initial salt concentration and the RH ratio) affect the crystallization temperature significantly. Increasing the initial salt concentration caused a drop of the crystallization temperature from 675 to 630° C. Such crystallization temperature may be determined by the degree of hydration and the short-range order of the amorphous materials.

Please replace paragraph [0051] of the specification with the following paragraph:

**[0051]** Using DTA, Macias et al. ("Kinetic Study of Crystallization in Zirconium Titanate from an Amorphous Reactive Prepared Precursor", *J. Non-Crys. Solids*,

147&148, 262-65, 1992) has conducted a careful kinetic study of crystallization in ZT from an amorphous precursor (hydroxoperoxo compound of Zr and Ti) precipitated by ammonia from titanium or zirconium methanol solutions containing hydrogen peroxide. The same crystallization kinetics model they used should apply to crystallization of other amorphous materials such as those obtained by dielectric-tuning coprecipitation. The reaction rate of a solid-state transformation, obeying a nucleation and growth process, should follow the Johnson-Mehl-Avrami (JMA) kinetic model. The simplified model with Doyle's approximation can be written as

$$\ln \left[ \ln \frac{1}{1-\alpha} \right] = n \ln \frac{AE}{\beta R} + 5.33 - 1.05 \frac{nE}{RT}$$

where  $\alpha$  is the reacted fraction,  $n$  is a parameter depending on the crystallization mechanism,  $A$  is the Arrhenius preexponential factor,  $E$  is the activation energy,  $\beta$  is the heating rate,  $R$  is the gas constant ( $=8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the absolute temperature. A plot of  $\ln[-\ln(1-\alpha)]$  vs.  $(1/T)$  should be a straight line of slope  $nE$ . For the ZT crystallization reaction from precursors, Macias et al. ("Kinetic Study of Crystallization in Zirconium Titanate from an Amorphous Reactive Prepared Precursor", J. Non-Crys. Solids, 147&148, 262-65, 1992) determined that  $n = 1.02$  which was explained by considering an agglomerated system constituted of a constant number of small particles as nuclei. In such a system, the rate of crystallization is controlled by random nucleation. Using the same method with the data shown in Fig. 8, we determined the activation energy  $E$  for our samples: 323 kJ/mol (for  $RH = 5/1$ ), 290 kJ/mol (for  $RH = 1/1$ ), 174 kJ/mol (for  $C = 0.2 \text{ M}$ ), and 139 kJ/mol (for  $C = 0.025 \text{ M}$ ). There seems to be a general trend of increase in activation energy with increasing  $RH$

and solution concentration C. The activation energies for crystallization from the precursor powders prepared by the method of the present invention are significantly lower than the value reported in the literature, i.e., 620 kJ/mol (Macias et al., "Kinetic Study of Crystallization in Zirconium Titanate from an Amorphous Reactive Prepared Precursor", *J. Non-Crys. Solids*, 147&148, 262-65, 1992). This means that the nanostructured precursor ZT powders of the present invention are much easier to crystallize.

Please replace paragraph [0054] of the specification with the following paragraph:

**[0054]** It was previously reported that when a high homogeneity level is not achieved, crystallization of  $\text{TiO}_2$  is observed before crystallization into  $\text{ZrTiO}_4$  (see Navio et al., "Formation of Zirconium Titanate Powder from a Sol-Gel Prepared Reactive Precursor", *J. Mater. Sci.* 27, 2463-2467, 1992; and Navio et al., "On the Influence of Chemical Processing in the Crystallization", *J. Mater. Sci. Lett.*, 11, 1570-1572, 1992 ~~1992a, 1992b~~), whereas homogeneous gels crystallize directly into  $\text{ZrTiO}_4$  below 700°C (see Bhattacharya et al., 1994, 1996b; "Low-temperature Synthesis and Characterisation of Crystalline Zirconium Titanate Powder", *Mat. Lett.* 18, 247-250, 1994; Bhattacharya et al., "Inorganic Sol Gel Synthesis of Zirconium Titanate Fibres", *J. Mater. Sci.*, 31, p. 5583-5586 1996; Isobe et al., "Mechanochemical Synthesis of  $\text{ZrTiO}_4$  Precursor From Inhomogeneous Mixed Gels", *Mater. Res. Soc. Symp. Proc.* 346, 273-277, 1994; Bonhomme-Courty et al., "Preparation of  $\text{Al}_2\text{TiO}_5\text{-ZrO}_2$  Mixed Powders via Sol-Gel Process", *J. Sol Gel Sci. & Technol.* 2, 371-375, 1994; Macias et al., "Kinetic

Study of Crystallization in Zirconium Titanate from an Amorphous Reactive Prepared Precursor", *J. Non-Crys. Solids*, 147&148, 262-65, 1992; McHale and Roth, "Low Temperature Phase Relationships in the System  $\text{ZrO}_2\text{-TiO}_2$ ", *J. Am. Ceram. Soc.* 69, 827-832, 1986). In the dielectric-tuning coprecipitation process of the present invention, using equal molar Zr and Ti in starting solution, no phase separation or impurity phase (anatase) was observed in any of the ZT samples, because all our ZT precursor particles are purely amorphous. It can be inferred that titanium tends to coprecipitate with equal moles of zirconium to form amorphous ZT compounds. Otherwise, titanium will form the undesirable anatase/brookite phase if it precipitates out alone. In fact, this homogeneity in molecular composition (in terms of the Zr/Ti ratio) has been verified by the TEM/EDS technique. The compositions at three different positions inside the microsphere (Fig. 9(a)) show almost identical composition. However, when the molar ratio  $\text{Ti/Zr} = 2$  was used in the initial mixture solution, it was observed the crystalline titania (anatase/brookite phase) in the as-prepared sample. With heat treatment from 27 to  $1200^\circ\text{C}$ , the rest of the amorphous phase in the titania-containing sample converts the  $\text{ZrTiO}_4$  phase while the titania phase coexists. Obviously, there is a certain tolerance of deviation from an equal molarity Ti/Zr ratio within which single-crystalline  $\text{ZrTiO}_4$  phase will form. Clearly, the ratio of  $\text{Ti/Zr} = 2$  is beyond this tolerance.

Please replace paragraph [0056] of the specification with the following paragraph:

**[0056]** The dielectric-tuning coprecipitation method of the present invention is different from the chemical precipitation reported by Leoni et al. ("Aqueous Synthesis

and Sintering of Zirconium Titanate Powders for Microwave Components”, J. Eur. Ceram. Soc., 21, 1739-41, 2001), although both process may use the same mixed zirconium and titanium salts. The chemical precipitation process is hard to control and inhomogeneous and produces precipitates in the form of nonsphere agglomerates. In contrast, the dielectric-tuning process generates a homogeneous nucleation and growth environment, is controllable by varying alcohol content and temperature, and produce precipitates consisting of dispersed, near-uniform-sized microsphere particles and nanosphere particles.